

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-331537
(43)Date of publication of application : 14.12.1993

(51)Int.Cl. C21D 8/02
C21D 9/46
C23C 2/06
C23C 2/28
// C22C 38/00
C22C 38/04

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(54) MANUFACTURE OF GALVANNEALED HIGH TENSILE STRENGTH COLD ROLLED STEEL PLATE EXCELLENT IN CORROSION RESISTANCE AND FORMABILITY

(57)Abstract:

PURPOSE: To obtain a method for manufacturing a galvanized steel plate having tensile properties such as high tensile strength, low yield ratio and high elongation as well as excellent in rustproofing force and used as an automotive steel plate or the like.

CONSTITUTION: Steel constituted of 0.05 to 0.3% C, $\leq 2\%$ Si, 2 to 3.5% Mn, 0.1% P and $\leq 0.1\%$ S, and the balance Fe is hot-rolled (at \geq Ar3 point finishing temp.) and is cold-rolled and thereafter, the cold rolled plate is applied with preplating (such as Fe-B plating). It is introduced into a continuous galvannealing line, is thereafter annealed at the Ac1 to Ac3 point (for 10 to 300sec holding time), is rapidly cooled from the temp. at $\geq 2^\circ\text{C}/\text{sec}$ average cooling rate to form a composite structure of an α phase and an α' phase and is galvanized and then, the plated layer is applied with an alloying treatment at 450 to 600°C.

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CLAIMS

[Claim(s)]

[Claim 1]C:0.05 to 0.3%, less than Si:2.0%, Mn : steel which consists of the remainder Fe and an inevitable impurity 2.0 to 3.5%, P:0.1% or less, and S:0.1% or less, In a continuous hot dip galvanizing line after hot-rolling and rolling round above an Ar_3 transformation point, cold-rolling, considering it as steel sheets after pickling treatment and performing pre plating of an iron system, In a temperature region of an Ac_1 - Ac_3 transformation point, after carrying out heating maintenance for 10 to 300 seconds, it cools to temperature below an Ms point with an average cooling rate at not less than 2 **/second, A manufacturing method of alloying hot-dip-zincing cold rolled high tensile strength steel sheets excellent in corrosion resistance and a moldability introducing into a hot-dip-zincing bath and carrying out alloying treatment after hot dip zincing in a 450-600 ** temperature region.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the manufacturing method of alloying hot-dip-zincing cold rolled high tensile strength steel sheets excellent in corrosion resistance useful as a steel plate for cars, etc., press-forming nature, etc.

[0002]

[Description of the Prior Art]Development of high intensity cold rolled sheet steel is wholeheartedly furthered for the purpose of the weight saving of the body, and the improvement in safety, and the steel plate for cars in recent years as a rustproof force remedy to the salt damage for the life extension of a car, etc., Alloying hot-dip-zincing cold rolled sheet steel attracts attention from points, such as the cost, rust prevention performance, and paintwork. A solid-solution-strengthening method make a crystalline lattice distorted in strengthening of cold rolled sheet steel by addition of penetration type dissolution elements, such as replaced type dissolution elements, such as Si, Mn, and P, C, N, A precipitation-strengthening method which adds carbon nitride formation elements, such as Ti, Nb, and V, and to which dispersed precipitation of the detailed carbon nitride is carried out, Complex tissue strengthening etc. which consider the crystalline structure of a steel plate as the organization which the hard martensitic phase distributed minutely uniformly to the elastic ferrite phase are known (JP,2-149642,A, JP,2-290955,A, JP,3-28325,A, JP,4-26744,A, etc.). The alloying hot dip zincing of cold rolled sheet steel introduces cold rolled sheet steel into a continuous hot dip galvanizing line, After performing continuous-annealing processing for removal of distortion, elasticity-izing, non-aging-izing, etc., It **** in a molten zinc bath, the zinc plating layer of predetermined coating weight is formed, and subsequently to an alloying treatment furnace it feeds, and is carried out by what is made for Fe and molten zinc to react by diffusion of Fe from a base steel sheet (a Fe-Zn alloy plating layer is formed).

[0003]

[Problem(s) to be Solved by the Invention]Although there are some methods in high intensity-ization of cold rolled sheet steel as mentioned above, Noting that the tensile strength obtained by a solid-solution-strengthening method is an about 30 to 45 kgf/mm² grade and I will obtain the high intensity which exceeds 50 kgf(s)/mm² by the law, If reinforcing elements, such as Si, Mn, and P, are added so

much, in a steelworker, the operability of each stage of a pickling process and a hot-dip-zincing process will get worse remarkably. Since oxide films generated on the cold-rolled-sheet-steel surface, such as Si and Mn, worsen plating wettability, and it becomes a cause which produces un-plating at a hot-dip-zincing process especially and the reaction velocity in alloying treatment becomes remarkably slow, It becomes what has heterogeneous processing not only taking a long time but Zn-Fe-alloy plating layer, and it becomes impossible to acquire expected corrosion resistance. When applying strengthening which used the precipitation-strengthening method together to a solid-solution-strengthening method, can obtain the high intensity exceeding about 60 kgf(s)/mm^2 as both synergistic effect, avoiding abundant addition of the above solid-solution-strengthening elements, and the inconvenience by it, but. Since it is accompanied by increase of a yield ratio on the other hand, it is inferior to the shape freezing nature in press forming, and the balance of intensity-elongation is not good, either.

[0004]On the other hand, when depending the crystalline structure of a steel plate on strengthening made into the complex tissue which consists of a ferrite phase and a martensitic phase, Fully attaining high intensity-ization exceeding 50 kgf(s)/mm^2 , comparatively high elongation and low yield ratio of high intensity can be obtained, and the difficulty of press forming is eased compared with strengthening which uses together the above-mentioned solid solution strengthening and precipitation strengthening, and it is advantageous also in respect of press shape freezing nature. However, it is the purpose of improving hardenability required for formation of the complex tissue containing a martensitic phase in the law, It is difficult to accompany the fall of plating nature (plating wettability, alloying treatment nature), and to secure sufficient corrosion resistance of alloying hot dip zincing in relation to the quantity of the addition of Si and Mn being increased, for this reason.

[0005]Thus, it was difficult to attain simultaneously high-intensity-izing of cold rolled sheet steel, and a corrosion-resistant improvement in the conventional manufacturing method. Then, this invention demonstrates the improvement effect of high-intensity-izing by complex tissue strengthening, a low yield ratio, and good strength - elongation balance to the maximum extent, and tends to improve plating nature and tends to provide the manufacturing method of the alloying hot-dip zinc-coated carbon steel sheet which can secure good corrosion resistance.

[0006]

[Means for Solving the Problem]A manufacturing method of alloying hot-dip-zincing cold rolled high tensile strength steel sheets of this invention, C:0.05 to 0.3%, less than Si:2.0%, Mn : steel which consists of the remainder Fe and an inevitable impurity 2.0 to 3.5%, P:0.1% or less, and S:0.1% or less, In a continuous hot dip galvanizing line after hot-rolling and rolling round above an A_{r3} transformation point, cold-rolling, considering it as steel sheets after pickling treatment and performing pre plating of an iron system, After carrying out heating maintenance for 10 to 300 seconds in a temperature region of an A_{c1} - A_{c3} transformation point, it cools to temperature below an M_s point with an average cooling rate at not less than $2^\circ\text{C}/\text{second}$, introduces into a hot-dip-zincing bath, and is characterized by carrying out alloying treatment in a $450\text{--}600^\circ\text{C}$ temperature region after hot dip zincing.

[0007]

[Function]After heating maintenance is carried out in a continuous hot dip galvanizing line at the annealing temperature of an $Ac_1 - Ac_3$ transformation point, the cold rolled sheet steel cooled from the temperature region with the average cooling rate at not less than $2^{\circ}\text{C}/\text{second}$, The complex tissue which the martensitic phase (α' phase) distributed minutely and uniformly with the quenching (hardening) all over the base which consists of ferrite phases (α phase) is formed. Since the surface of the cold rolled sheet steel has the good plating nature (plating wettability, alloying treatment nature) by iron system plating performed as pre plating, In the alloying treatment, it is short-time processing, and a hot-dip-zincing layer without un-plating is formed, and Zn-Fe-alloy-ized reaction can be attained, without being accompanied by the nonuniformity of excess and deficiency. The alloying hot-dip zinc-coated carbon steel sheet manufactured by this invention, Corrosion resistance by homogeneous Zn-Fe-alloy plating layer which does not exceed 0.65, has a low yield ratio which fully fills 0.60 or less, and not less than 15% of high elongation, and does not have un-plating with the intensity level more than 60 kgf/mm tensile strength² excelled and stabilized is **** (ed).

[0008]Hereafter, this invention is explained in detail. The reason for limitation for the chemical composition of steel in this invention is as follows. All % that show the content of an element are weight %.

C:0.05 to 0.3%C dissolves in steel, and raises the intensity of steel. It is because the improving strength effects run short and it becomes impossible to secure the intensity level more than 60 kgf/mm tensile strength², when there is having made [less] the minimum of content into 0.05% than this. The maximum was made into 0.3% because ductile shortage would be caused and press-forming processing would become difficult, if this was exceeded.

[0009]Having limited the maximum of the content of Si to 2.0% Si:2.0% or less, It is because the fall of plating wettability by generation of the oxide film of a steel sheet surface and the fall of the alloying treatment nature of hot dip zincing are remarkable, and it becomes impossible to fully prevent it if this is exceeded even if degradation of the plating nature performs pre plating of an iron system. It is 1.5% or less preferably. Since Si is an element which has solid solution strengthening and the hardenability improvement effect of steel and the existence does not serve as hindrance of reservation of a low yield ratio, It makes that it is effective in raising intensity, and preferably into 0.02 to 1.5% to adjust the content by 2.0% or less which does not check plating nature of within the limits.

[0010]Mn: 2.0 to 3.5%Mn is an element which has a hardenability improved effect of steel. It is because it becomes impossible to fully attain high intensity-ization by the generated amount of the martensitic phase occupied all over complex tissue with shortage of the hardenability of steel having been insufficient for having made the minimum of content into 2.0% in a small quantity, and having considered it as complex tissue from it and becomes a cause of increase of the yield ratio of a steel plate. On the other hand, 3.5% was made into the maximum because the generated amount of a martensitic phase became superfluous, ductile shortage would be caused and press-forming nature would worsen, if the quantity of Mn was increased exceeding this.

[0011]Content of P:0.1%or less P was made into 0.1% or less in order to prevent the fall of the processability by embrittlement of steel. Preferably, it is 0.05% or less. But since P is an element

which has a solid-solution-strengthening operation, it is effective in raising the intensity of steel to make 0.01% or more of P contain in proper quantity within limits which do not cause degradation of processability. Although existence of P controls diffusion of the Fe atoms in the alloying treatment of hot dip zincing and becomes the cause of reducing alloying treatment nature, even if it makes a little above-mentioned P exist, it does not produce actual harm in alloying treatment in this invention to which it is being supposed that pre plating of an iron system is performed.

[0012]Since S:0.1% or less S causes embrittlement of steel and degrades processability, it must not exceed 0.1%. Preferably, it is 0.05% or less.

[0013]Next, hot-rolling of the steel which has the above-mentioned chemical composition, and each process of following it are explained. We decided to make finishing temperature in hot-rolling more than an Ar_3 transformation point, and to perform hot-rolling in a gamma-phase temperature region in order to make the construction material improvement effect of steel fully reveal.

If hot-rolled in the two-phase temperature region (Ar_1 - Ar_3) where alpha phase was intermingled in gamma-phase, it is because the fall of the intensity of a final product steel plate or processability is caused.

Hot rolled sheet steel is rolled by the cold rolled sheet steel of predetermined board thickness with cold rolling after pickling treatment.

[0014]We decided to precede introducing cold rolled sheet steel into a continuation hot-dipping line, and to perform pre plating of an iron system to the surface in order to improve the plating nature of a steel plate. That is, since steel in this invention has the presentation containing comparatively a lot of Mn as January the 15th of the lunar calendar matter for hardenability, the surface of cold rolled sheet steel tends to generate the oxide film of Mn, therefore its plating nature (plating wettability, alloying treatment nature) is not enough as it is. The plating nature of this steel sheet surface improves by performing pre plating of an iron system. Electroplating can perform the pre plating. Although the plating presentation may be pure iron, since especially the Fe-B alloy plating containing optimum dose of B (about 10-30 ppm) has the good familiarity by molten zinc, it is preferred. The coating weight of pre plating is good to use more than about 0.5 g/m^2 (per one side), in order to make the effect into sufficient thing, but even about 5 g/m^2 (per one side) is enough as it.

[0015]We decided to anneal the cold rolled sheet steel which performed pre plating of an iron system and was introduced into continuation hot dip zincing in the temperature region of an Ac_1 - Ac_3 transformation point in order to make the two-phases coexisting organization of alpha+gamma generate.

Between the heating maintenance was made into 10 seconds or more in order to fully carry out dissolution concentration of the January the 15th of the lunar calendar matter for hardenability, such as Mn, Si, and C, into gamma-phase.

having made the maximum of retention time into 300 seconds -- within a time [the] -- gamma-phase dissolution of the above-mentioned element -- it is because concentration is completed mostly, and is because it not only reduces line efficiency, but the prolonged heating maintenance exceeding it causes a fall of the formation of grain growth big and rough, and the material property based on it.

Annealing (distortion removal, softening, non-aging-izing, etc.) of cold rolled sheet steel is also

simultaneously attained by this heating maintenance.

[0016]After carrying out heating maintenance in the two-phase temperature region of an $Ac_1 - Ac_3$ transformation point, cooling from the temperature region is considered as quenching in order to make gamma-phase metamorphose into a martensitic phase (α' phase) and to form the complex tissue of an α phase + α' phase.

It is because it becomes impossible for having made the average cooling rate into a second in not less than 2×10^{-3} /to secure the complex tissue which a transformation to bainite arises and consists of an α phase and an α' phase in a cooling rate lower than it.

[0017]The cold rolled sheet steel in which complex tissue was introduced is ****(ed) by the hot-dip-zincing bath, predetermined plating is performed, the alloying treatment furnace subsequently to 450-600 °C held ****, and alloying of a zinc plating layer is performed. The conditions that a hot-dip-zincing process is special are not added, but what is necessary is just to perform them in accordance with a conventional method, and a uniform zinc plating layer without un-plating is formed of the good wettability according [the surface] to iron system pre plating. Since alloying treatment nature is also good as an effect of pre plating, a predetermined alloying reaction can be completed by short-time processing. The treatment temperature was not less than 450 °C in order to urge the counter diffusion of Fe and Zn atom and to use the whole plating layer as homogeneous Fe-Zn alloy without excess and deficiency efficiently.

It is because the martensitic phase in the complex tissue of a steel plate will be annealed and having made 600 °C of another side into the maximum will cause degradation of a material property, especially tensile strength and a ductile fall, if it is exceeded.

[0018]

[Example]

[I]The steel which has the chemical composition shown in the manufacture table 1 of a test specimen was used as the hot rolled sheet steel of 2.0 mm of board thickness with hot-rolling, cold rolling was given after pickling treatment, and the cold rolled sheet steel of 0.8 mm of board thickness was obtained. After performing Fe-B plating (B content: 15 ppm) by electroplating to cold rolled sheet steel as pre plating, It introduced into the continuous hot dip galvanizing line, and annealing which carries out heating maintenance, and quenching (hardening) processing from the temperature were performed in the $Ac_1 - Ac_3$ transformation-point-temperature region, it ****(ed) to the hot-dip-zincing bath (bath temperature: 460 °C), predetermined plating was performed, and, subsequently alloying treatment was performed. The finishing temperature in hot-rolling, the pre plating coating weight of cold rolled sheet steel, the annealing conditions (temperature, time) in a continuation plating line, the cooling rate from annealing temperature, the plating coating weight of hot dip zincing, and alloying treatment conditions (temperature, time) were written together to Table 1. The Ar_3 transformation point of the steel plate of a test specimen is about 700 °C, and an $Ac_1 - Ac_3$ transformation-point-temperature region is about 700-800 °C.

[0019][II]About various-characteristics each test specimen, tensile various characteristics were

measured, and unplated existence and the alloying state (excess and deficiency of Zn-Fe-alloy-ized reaction, existence of surface abnormalities) of the plating layer were evaluated as plating quality, and the result shown in Table 2 was obtained. "O" of the column un"plated" has good plating wettability among Table 2, and there is no un-plating, Mean that un-plating generated "x" with the shortage of plating wettability, and "O" of the "alloying state" column, It means that cover all the surfaces of a plating layer and homogeneous Zn-Fe-alloy-ization is attained, and that "x" has caused the abnormalities in surface appearance by that shortage of an alloying reaction or a reaction progresses too much and it.

[0020]No.1 - 5 are comparative examples among front, and the example of an invention, No.101 - 106 comparative example No.101 and No.102, The example and No.103 which omitted iron system pre plating of cold rolled sheet steel, The example which is too high, the example which is [No.105] too low, and No.106 are examples which are too low.

[0021]Though tensile strength exceeds 60 kgf(s)/mm^2 greatly, and each of steel plates of No.1 which is an example of an invention - 5 has an intensity level more than 75 kgf/mm^2 and is high intensity, a yield ratio is as low as 0.45 or less enough, and, moreover, possesses not less than 15% of high elongation. Also about plating quality, as an effect of pre plating, there are no excess and deficiency of un-plating or an alloying reaction, and healthy Zn-Fe-alloy plating layer is formed.

[0022]On the other hand, if comparative example No.101 - 106 are seen, although No.101 and No.102 have the tractive characteristics of example Noof invention .1 - 5, and an equivalent level, since pre plating is omitted, the plating nature of a steel plate is bad and has caused un-plating and poor alloying. Like No.102, the poor alloying (shortage of an alloying reaction) is nonavoidable, even if it sets up alloying treatment temperature to the limit of the maximum.

[0023]No.103 which is insufficient of Mn contents, Although it has the tensile strength more than 60 kgf(s)/mm^2 once, as a result for which hardenability was insufficient with shortage of a Mn content, In spite of having received predetermined annealing and rapid cooling treatment, the yield ratio is remarkably high compared with 0.76 and the example of an invention, and inferior to press shape freezing nature. Although shortage of a Mn content does not have No.104 unlike No.103 and proper chemical composition is given, Since annealing of the steel plate was performed at the temperature (gamma-phase temperature region) exceeding an Ac_3 transformation point, as a result in which predetermined complex tissue was not formed, a yield ratio is remarkably [as 0.79] high, and tensile strength also remains in the low level compared with it of the example of an invention.

[0024]Although No.105 is [the chemical composition of steel] proper, since it is insufficient of the cooling rates from annealing temperature, a yield ratio is remarkably [as 0.85] high, and tensile strength also runs short of [circumference of lower] elongation greatly in the intensity level of the example of an invention. The cause in this example that plating quality is poor is because alloying treatment time became long in relation to having lowered line velocity after [required] cooling-rate adjusting after annealing of a steel plate, and the alloying reaction advanced superfluously, and is not based on the defect of the pre plating effect of a steel plate. Although No.106 has the improved tractive characteristics equivalent to the example of an invention and un-plating is prevented as an effect of pre plating, since alloying treatment temperature is low, the poor plating quality by shortage

of an alloying reaction has been caused.

[0025]

[Table 1]

No.	銅の化学組成, wt %					熱延仕温上度 (°C)	ブ レ ッ 着 め き 量 (g/m ² 片面)	焼 鈍		平均 冷却 速度 (°C/秒)	垂 鉛 め き 量 (g/m ² 片面)	合金化処理	
	C	Si	Mn	P	S			温 度 (°C)	時 間 (秒)			温 度 (°C)	時 間 (秒)
1	0.12	0.24	2.04	0.021	0.004	900	0.5	780	50	2.6	4.5	550	30
2	0.11	0.27	2.10	0.024	0.003	900	1.0	780	50	2.6	4.5	500	30
3	0.12	0.21	2.20	0.030	0.004	900	2.0	790	50	2.6	4.5	500	30
4	0.12	0.20	2.11	0.021	0.005	900	2.0	780	50	2.6	4.5	550	30
5	0.12	0.23	2.13	0.024	0.002	900	2.0	770	50	2.6	4.5	550	30
101	0.11	0.24	2.09	0.028	0.004	900	—	780	50	2.6	4.5	550	30
102	0.11	0.26	2.05	0.022	0.004	900	—	780	50	2.6	4.5	600	30
103	0.13	0.25	1.20	0.020	0.003	900	2.0	780	50	2.6	4.5	550	30
104	0.11	0.26	2.01	0.030	0.005	900	2.0	850	50	2.6	4.5	550	30
105	0.11	0.29	2.15	0.022	0.004	900	2.0	780	100	1.3	4.5	550	60
106	0.12	0.28	2.10	0.028	0.004	900	2.0	780	50	2.6	4.5	400	30

[0026]

[Table 2]

No.	引 張 特 性				め っ き		
	引 張 強 さ (kgf/mm ²)	降 伏 点 (kgf/mm ²)	降 伏 比	伸 び (%)	不 め っ き	合 金 化 状 態	
1	79.2	33.4	0.42	18.0	○	○	発 明 例
2	80.7	33.7	0.42	17.2	○	○	
3	76.5	33.3	0.44	16.0	○	○	
4	80.9	32.7	0.40	20.5	○	○	
5	81.5	36.8	0.45	15.4	○	○	
1 0 1	80.0	34.5	0.43	15.7	×	×	比 較 例
1 0 2	80.3	36.1	0.45	16.1	×	×	
1 0 3	61.5	47.0	0.76	8.5	○	○	
1 0 4	64.7	51.1	0.79	10.1	○	○	
1 0 5	60.9	52.1	0.85	9.0	○	×	
1 0 6	79.9	39.0	0.49	16.8	○	×	

[0027]

[Effect of the Invention]The alloying hot-dip zinc-coated carbon steel sheet manufactured by this invention method has a tensile strength level exceeding 60 kgf/mm², and it is provided with the advanced rustproof force by healthy plating quality. Though it is high intensity, it has a low yield ratio and high elongation, and press-forming processing is easy and excellent also in shape freezing nature. Therefore, it is suitable as a high tension rustproof steel plate for responding, for example to the request of the body weight saving of a car, the improvement in safety, life extension, etc., etc.

[Translation done.]